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The Dependence of Relative Enhancement of SERS Bands on Temperature

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Abstract: The adsorption and binding behavior of 2,5-dimercapto-1,3,4-thiadizole (DMTD) on silver surface was studied by near-infrared Fourier Transfer surface enhanced Raman scattering (NIR FT-SERS) technique. It was found that the relative intensities of the SERS bands change regularly with the increasing of temperature, which suggests the transformation of the tautomers or the re-orientation of DMTD molecules in the surface layer.

Key words: Surface enhanced Raman scattering (SERS), 2,5-dimercapto-1,3,4-thiadiazole (DMTD), Adsorption and binding, Relative intensity, Transformation

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SERS has been explored both theoretically and experimentally since Fleischmann first discovered it at 1974[1], and new results under different conditions are continuously reported. In this presentation, the dependence of the relative intensities of SERS bands on temperature is investigated. The changes of the Raman band intensity may be used to analyze the variation of the relative content of different species, or to investigate the transformation of the orientation of adsorbents on the substrate surface, etc. For example, Mukherjee found that 2-bromothiophene could

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form a monolayer on the silver surface at the concentration of 10^{-3} mol/L[2].

In our laboratory, we found that the relative intensities of the two SERS bands at 1 412 cm^{-1} and 1 367 cm^{-1} of 2,5-dimercapto-1,3,4-thiadiazole (DMTD) adsorbed onto the silver surface, have an interesting transformation process.

1 Experimental Section

1.1 Materials and sample preparation methods

The silver samples were prepared from the Ag 99.99 % foil, 0.025 mm thick. 2,5-dimercapto-1,3,4-thiadiazole (DMTD) was synthesized in our laboratory[3], recrystallized twice, mp 162～163 ℃. Ethanol used was of analytical grade. The water was purified by double distillation.

Electrochemical roughening of the silver surface was carried out in a typical three-electrode potential static system. A platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials are reported with respect to SCE.

The silver foil was first polished mechanically, and then electrochemically roughened in 0.1 mol/L KCl solution by 5 oxidation-reduction cycles (ORC) between - 0..6～0.0 V, washed repeatedly with distilled water after withdrawing. Finally, it was immersed in the alcoholic solutions of DMTD in different concentrations for 5 min to allow the monolayer to form. Then it was rinsed in ethanol to remove the physisorbed substance, dried in air for the lateral measurements.

1.2 Instrumental and experimental configurations

SERS spectra were obtained with a (Germany) Bruker system RFS-100 FT-Raman spectrometer equipped with a diode-pumped Nd-YAG laser emitting at a wavelength of 1 064 nm. The laser power at the sample was 150 mW for the silver foil. The spectral resolution of the Raman spectrometer was 4 cm^{-1}. The scattered light was at an angle of 180°. All of the data were dealt with the OPUS 2.0 software systems.

2 Results and Discussion

Fig. 1 shows the SERS spectra of DMTD adsorbed onto the silver surface at different temperatures. In Fig. 1, we find that the two SERS bands at 1 412 cm^{-1} and 1 367 cm^{-1} display regular changes. In the temperature range, the relative intensities of the two bands change dramatically in converse manner. At lower temperature, 25 ℃ for example, there appears one band at 1 412 cm^{-1} in Fig. 1a, and the 1 367 cm^{-1} band is too weak to be seen. While at 190 ℃, the higher temperature, we find a strong band at 1 367 cm^{-1} with a very weak shoulder at 1 412 cm^{-1} in Fig. 1g. At 140 ℃, the two bands have similar intensities.

In order to see clearly and in detail the changes of the two bands at 1 412 cm^{-1} and 1 365 cm^{-1}, we plotted the plot of the temperature dependence of the relative intensity of the two SRES bands, which is shown in Fig. 2. In general, we find that the intensity of the 1 412 cm^{-1}

band decreases, while the other band at 1 367 cm^{-1} increases with increasing temperature, though they do not change as smoothly as we formerly considered.

DMTD has three tautomers in the solid state and it exists primarily in the thiol–thione form[4,5]. Fig. 3 shows the normal Raman spectrum of DMTD in solid state. It is easy to find that characteristic band of υ_{S-H} band at 2 487 cm^{-1} in Fig. 3 disappeared in Fig. 1. This indicates that DMTD was chemisorbed onto the silver surface. The sulphide salt of DMTD was formed at the same time, which can also be evidenced in another point. In Fig. 1f, at 162 ℃, the melting point of DMTD, there are still strong SERS bands, which also suggests the adsorption behavior is a chemical one, and new products formed during the adsorption process whose melting point is higher than 190 ℃. Otherwise, DMTD should have already decomposed and we could not find any SERS signals any more.

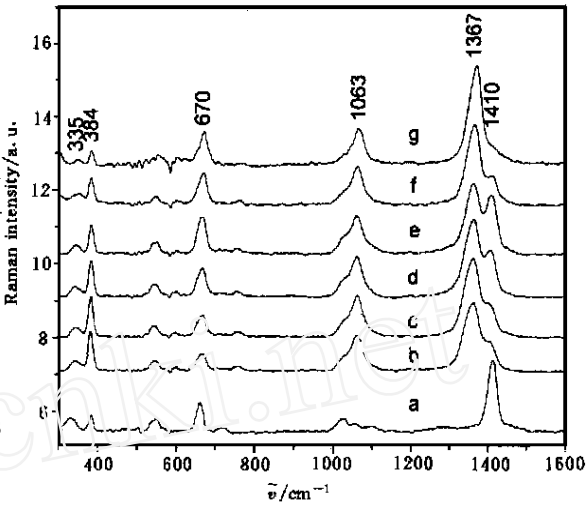

Fig. 1 The SERS spectra of DMTD adsorbed onto the silver surface at (a) 25 ℃ and after being heated for 3h at (b) 50 ℃, (c) 80 ℃, (d) 110 ℃, (e) 140 ℃, (f) 162 ℃, (g) 190 ℃. The concentration of the solution is 10^{-1} mol/L

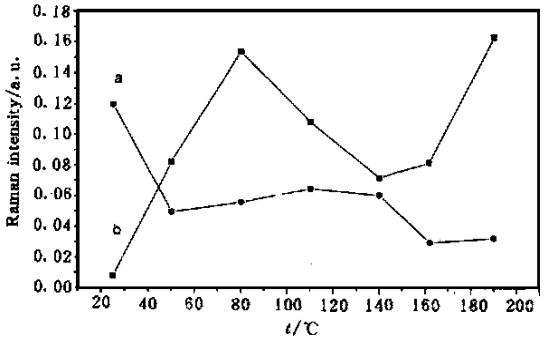

Fig. 2 Temperature-dependence of the relative enhancement of the SERS bands at (a) 1 412 cm^{-1} and (b) 1 367 cm^{-1}

In Fig. 2a, the very strong band at 1 412 cm^{-1} indicates that the product is the mono-sulphur salt of DMTD[6]. While in Fig. 2b, the strong band at 1 367 cm^{-1} suggests the formation of the disulfide salt of DMTD[6]. So it is clear that there is an equilibrium shifting between the two products, and it is the heating process that makes the transformation of the two tautomers. At 25 ℃, a lower temperature, DMTD chemisorbed on the silver surface through one of its two mercapto groups. However, when the sample was heated at 190 ℃ for 3h, DMTD chemisorbed onto the silver surface via both of its two mercapto groups. Especially at 162 ℃, the melting point of DMTD, the intensity of the band at 1 367 cm^{-1} appeared for the second time. So 162 ℃ is a proper temperature for the prod-

uct of DMTD to transform from the monosulfide salt to the disulfide salt. At the higher temperature, we find that most of the DMTD molecules exist in the dithiol form on the silver surface, and only a very small amount of DMTD molecules exist in the thiol–thione form.

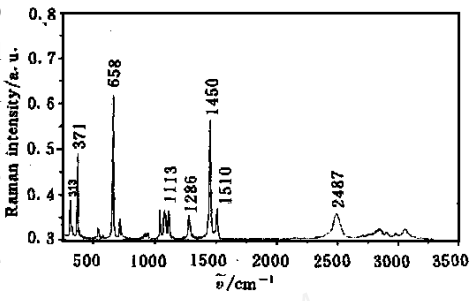

Fig. 3　The normal Raman spectrum of DMTD in the solid state

It is reasonable that at lower temperature, as the concentration is high, the main product of the chemical adsorption process is the monosulfide salt of DMTD. However, the monosulfide salt of DMTD still has another active site. That is to say, the thiocarboxyl group can tautomerize into the mercapto group and can react further with the silver atoms. It tends to transform to the disulfide salt because it is more stable in energy than the monosulfide one. When the samples were heated, the reactions continued gradually. Then the monosulfide salt of DMTD began to transfer into the disulfide salt, until finally nearly all of the species on the silver surface are the disulfide.

The other two bands at 1 063 cm^{-1} and 670 cm^{-1} are due to the ring mode and the stretching vibration of C–S–C in the heterocyclic ring, respectively. Based on the above discussion together with the surface selection rules[7~9], we know that at lower temperature, DMTD chemisorbed on silver surface in the thiol–thione form. While at higher temperature, the chemisorbed DMTD exists in the dithiol form.. In both cases, the heterocyclic ring plane is perpendicular to the silver surface. The adsorption state of DMTD molecules on silver surface transferred from the monosulfide form to the disulfide form[10].

Based on the above discussions, we can conclude that the relative intensities of the SERS bands change dramatically with the temperature, which indicates the transformation of the tautomers or the re-orientation of DMTD molecules in the surface layer.

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表面增强拉曼散射峰相对强度与温度的关系

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摘要: 用近红外傅立叶变换表面增强拉曼散射技术研究了 2,5-二巯基-1,3,4-噻二唑(DMTD)在银表面的吸附与键合行为. 峰的相对强度随温度呈现出规律性的变化,表明 DMTD 异构体的相互转变或表面膜中 DMTD 分子的重新排布.

关键词: 表面增强拉曼散射(SERS);2,5-二巯基-1,3,4-噻二唑(DMTD);吸附与键和;相对强度;转变